''Perovskite oxide-based High Performance Electrochemical Supercapacitors''

Synopsis in Candidature for the Degree of

Doctor of Philosophy

Submitted by

Mr. Yaser Abdo Mohammed Noman AL-Hasani

Under the guidance of

Dr. Vijaykumar V. Jadhav

School of Physical Sciences

Submitted to

Swami Ramanand Teerth Marathawada University, Nanded

2021-2022

1. Introduction

The dense industrialization of human civilization and a rapid growth of the global population have put enormous strain on the environment and raised serious concerns about an impending energy crisis. Energy is of great importance in our daily lives. In order to meet the worldwide challenges of a sustainable supply of low-cost and clean energy, it is very important to have continuous innovation that should be driven by energy technologies, specifically generation, storage, and delivery systems [1-3]. Energy storage devices such as electrochemical supercapacitors, lithium-ion batteries, and fuel cells may be an ideal energy system for the future needs [4-6].

The supercapacitor is a significant type of electrochemical energy storage device which is also named electrochemical capacitors that has garnered worldwide attention due to its high power density in comparison to traditional capacitors and batteries, and long cycle life (> 100 000 cycles) in comparison to lithium ion batteries, and has been successfully applied in several important fields, such as electric vehicles (EV's) and electronic gadgets [7-10]. Therefore, myriad researchers working on the development of supercapacitor combine the properties of supercapacitor i.e. a high power density, long cycle, fast charging rate, and high energy density [11-12] with battery i.e. high energy density. Utilization of nanostructured electrode materials for storing charges is a common energy storage mechanism for batteries that may be impressive for supercapacitive electrode materials. Nevertheless, the nanostructured electrode materials often lead to a low packing density of the electrode, resulting in poor volumetric energy density [13-17]. In the current energy storage market, commercial production of supercapacitors is based on the densely packed, high-surface area of electrode materials. Due to large surface area perovskite oxides, of inherently densely packed structures, adduced tremendous scope as advanced electrode materials for supercapacitor applications [18].

2. Literature Review

Perovskite oxides with the general formula of ABO_3, originating from $CaTiO_3$, are a family of oxides [19]. Perovskite oxides have quickly drawn demanding attention owing to their low

cost, robust skeleton structure, high tap density, and inherent nature of containing oxygen vacancies and distinctive chemical tailoring [20]. Over the past few years, perovskite oxides have traditionally been used as functional materials in energy-related fields. The application of perovskite oxides grows rapidly, and more feasible ways to modify their performance in supercapacitor (SCs) SCs are being developed [21-23]. Till date, few researchers worked on perovskite oxides for energy conversion and storage applications have been published [24-25]. However, there is still a lack of application and performance and development of perovskite oxides needs to be studied in supercapacitor. Benefiting from the stable structure that accommodates abundant oxygen vacancies, perovskite oxide has a long cycling life with high energy storage capacity. Therefore, by considering and reviewing the properties of perovskite oxides, it is planned to synthesized $BiFeO_3$, $BaTiO_3$, and $LaCoO_3$ electrode materials using one of the following appropriate chemical methods for fabricating supercapacitor devices.

3. **Objectives**

The main objective of this synopsis is to develop and synthesis perovskite oxides for high performance supercapacitor devices.

- Synthesis of perovskite oxide active electrodes such as $BiFeO_3$, $BaTiO_3$, and $LaCoO_3$nanostructures using appropriate chemical synthesis method.
- Structural and morphological properties of the prepared nanostructured electrodes will be studied using various characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, etc.
- Electrochemical performance will be studied in various electrolyte solutions for better performance.
- Rate capability and capacitance retention will be studied and reported.
- Symmetric/asymmetric devices will be designed for exploratory.

4. Methodology

Several methods in the literature are used for the synthesis of Perovskite oxides such as Chemical Bath Deposition, successive ionic layer adsorption and reaction (SILAR), hydrothermal method, which are reliable and economic.

4.1 Chemical bath deposition

Chemical bath deposition (CBD) is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on variety of substrates by the controlled precipitation of the compounds from the solution. It is free from the high voltage equipment, works at room-temperature, and inexpensive. The only requirement for this deposition route is an aqueous solution consisting of a few common chemicals and a substrate for the film to be deposited. By optimizing preparative parameters, such as deposition temperature, time, pH, complexing agent etc.,

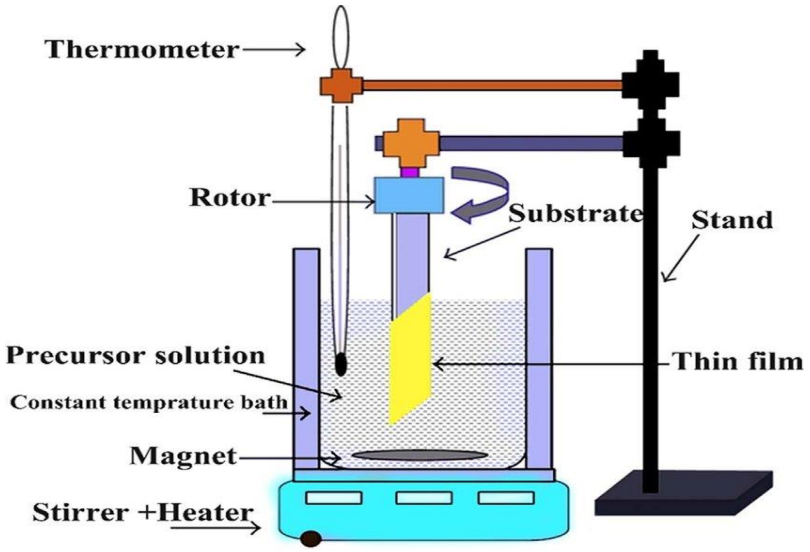

Fig.1. Instrumental details of CBD

4.2 Successive ionic layer adsorption and reaction

Successive ionic layer adsorption and reaction (SILAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition.

1. It is a process in which the deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles.
2. Relatively uniform films can be obtained on substrates of any shape; there is no restriction on substrate material, dimensions or its surface profile.

3. Unlike vacuum-based deposition methods, SILAR method does not require any expensive and sophisticated instruments and also vacuum at any stage which is a great advantage in the context of an industrial application.
4. The SILAR method usually operates at lower operating temperature i.e.≤ 100°C.

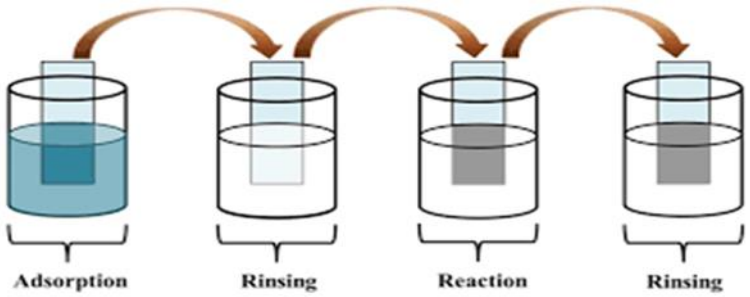

Fig. 2. Schematic representation of SILAR method.

4.3 Hydrothermal

Several nanomaterials are being successfully synthesized by using hydrothermal method. Nanomaterials with high vapor pressures can be produced by the hydrothermal method with minimum material loss. The compositions of nanomaterials to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions.

Other methods will be adopted if necessary.

5. Characterizations

A concise account of the instruments and techniques used for acknowledgement of structural, morphological, electrochemical properties, are discussed in this section.

4.4.1 Structural studies

X-ray diffraction (XRD) technique is a one of the influential, renowned and most appropriate techniques for structural revelation of materials prepared in the form of either films or powders.

4.4.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibration, rotational, and other low-frequency modes in a system.

4.4.3 Fourier Transform Infrared Spectroscopy

FT-IR spectroscopy is a tool for investigation of the various chemical groups present in the sample material.

4.4.4 Morphological studies

Field-Emission Scanning Electron Microscopy is a tool for investigation of the surface morphology and posture of the sample material.

4.4.5 High-Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM is one of most powerful techniques used in the characterization of nano-material. It has capacity to inspect the constitutional characteristics of nanocomposites such as grain shape and size, crystallinity and chemical variations at a nanometer scale resolution.

4.4.6 Electrochemical analysis

The cyclic-voltammetry (CV), Galvanostatic charge-discharge (GCD), stability, rate capability, and impedance spectroscopy will be measured using electrochemical work station.

6. ***Work plan***

The proposed work will be carried out through following phases:

Phase – I (First Year)

- In the first year, literature survey will be carried out. The various perovskite oxides will be prepared using suitable synthesis method.

Phase – II (Second Year)

- The electrochemical performance of the prepared perovskite oxides will be measured and studied in different electrolyte such as KOH, H_2SO_4, NaOH, and KCL, etc.

Phase – III (Third Year)

- To the study the industrial potential of the prepared perovskite oxides, the symmetric /asymmetric device will be fabricated.
- The work will be communicated time to time with the high impact journals.

7. References

1. Y. Liu, J. Dinh, M. O. Tade, Z. Shao, ACS Appl. Mater. Interfaces 8 (2016) 23774−23783.
2. D. A. Finkelstein, H. D. Abruna, ACS Energy Letters 2 (6) (2017)1439-1443.

3. C. Zhang, L. Zhang, G. Yu, Accounts of Chemical Research 53 (2020) 1648-1659.
4. S. Jang, H. Min, S. B. Cho, H. W. Kim, W. Son, C. Choi, S. Chun, C. Pang, Nano Letters 21, 16 (2021) 7079-7085.
5. K. Hikima, Y. Hinuma, K. Shimizu, K. Suzuki, S. Taminato, M. Hirayama, T. Masuda, K. Tamura, R. Kanno, ACS Applied Materials & Interfaces 13, 6 (2021) 7650-7663
6. C. A. Bessel, K. Laubernds, N. M. Rodriguez, R. Terry K. Baker, Journal of Physical Chemistry B 105 (2001) 1115-1118.
7. Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn, R. B. Kaner, Chemical Reviews 118 (2018) 9233-9280
8. M. P. Browne, E. edondo, M. Pumera, Chemical Reviews 120 (2020) 2783-2810
9. H. Wang, W. Wang, H. Wang, X. Jin, H. Niu, H. Wang, H. Zhou, T. Lin, ACS Applied Energy Materials 1 (2) (2018) 431-439
10. M. Tomy, A. A. Rajappan, V. M. Vimuna, X. T. Suryabai, Energy & Fuels, 2021, DOI: 10.1021/acs.energyfuels.1c02743
11. S. I. Kim, J. H. Kang, S. W. Kim, J. H. Jang, Nano Energy 39 (2017) 639−646.
12. N. Tang, H. You, M. Li, G. Z. Chen, L. Zhang, Nanoscale 10 (2018) 20526−20532.
13. A. Ramadoss, K. N. Kang, H. J. Ahn, S. I. Kim, S. T. Ryu, J. H. Jang, J. Mater. Chem. A 4 (2016)4718.
14. S. I. Kim, J. S. Lee, H. J. Ahn, H. K. Song, J. H. Jang, ACS Appl. Mater. Interfaces 5 (2013) 1596−1603.
15. L. Shen, L. Yu, X. Y. Yu, X. Zhang, X. W. Lou, Angew. Chem., Int. Ed. 54 (2015) 1868−1872.
16. S. I. Kim, S. W. Kim, K. O. Jung, J. B. Kim, J. H. Jang, Nano Energy 2016, 24, 17−24.
17. J. Yan, S. Li, B. Lan, Y. Wu, P. S. Lee, Adv. Funct. Mater. 30 (2020) 1902564.
18. K. N. Kang, H. Lee, J. Kim, M. J. Kwak, H. Y. Jeong, G. Kim, J. H. Jang, ACS Energy Lett. 5 (2020) 3828−3836.
19. J. P. Attfield, P. Lightfoot, R. E. Morris, Dalton Trans., 44 (2015) 10541-10542
20. P. Tan, M. Liu, Z. Shao and M. Ni, Adv. Energy Mater., 7 (2017) 1602674.
21. A. K. Tomar, A. Joshi, G. Singh, R. K Sharma, J. Mater. Chem. A 8 (45) (2020) 24013−24023.
22. K.-N. Kang, H. Lee, J. Kim, M. J. Kwak, H. Y. Jeong, G. Kim, J. H. Jang, ACS Energy Lett. 5 (2020) 3828−3836.
23. M. Rudra, H.S. Tripathi, A. Dutta, T. P. Sinha, Mater. Chem. Phys. 258 (2021) 123907.

24. W. J. Yin, B. Weng, J. Ge, Q. Sun, Z. Li and Y. Yan, Energy Environ. Sci., 12 (2019) 442–462.

25. J. Hwang, R. R. Rao, L. Giordano, Y. Katayama, Y. Yu and Y. Shao- Horn, Science, 358 (2017) 751–756.

Signature
Research Student

Signature
Research Supervisor/Guide/Co-guide
Department of Physics,
Shivaji Mahavidyalaya, Udgir, Dist. Latur
Maharashtra 413 517